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KINETIC STUDY OF SURFACE NUCLEATED $MgO-CaO-Al_2O_3-SiO_2$ GLASSES

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The paper investigated, by means of thermal analysis measurements, the validity of three different methods for the evaluation of the activation energy of crystallization for surface nucleated glasses belonging to the $MgO-CaO-Al_2O_3-SiO_2$ system, separating anorthite and diopside crystals. The values obtained from Kissinger equation of the activation energy for crystallization are comparable with those obtained by other authors for similar glassy systems, 90 to 150 kcal/mol. The results of the kinetic analysis using single-crystallization-peak method should be corrected taking into account the dimensionality of crystal growth.

Keywords: kinetics, $MgO-CaO-Al_2O_3-SiO_2$ glasses

Introduction

The nucleation and crystallization of glasses are important processes which need to be known in order to prepare glass-ceramics with desired microstructure and properties. The kinetic of the crystallization has been investigated by means of differential thermal analysis, DTA, and many parameters, such as crystallization temperature and activation energy, can be evaluated by different analytical models [1–8].

The purpose of this work is to verify the validity of three of these methods [1–6] for surface nucleated glasses from the $Mg-CaO-Al_2O_3-SiO_2$ glassy system previously investigated [9]. These glasses separate anorthite and diopside crystals during heating and since no nucleating agents were added only one heating treatment was required for the crystal growth, which started from the surface and moved toward the inside of the glass in form of two-dimension crystals [9].

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Experimental

Two different compositions: $0.2MgO–0.25CaO–0.05Al_2O_3–0.5SiO_2$ and $0.14MgO–0.25CaO–0.11Al_2O_3–0.5SiO_2$ (mol%) (hereafter abbreviated as A and B, respectively), were prepared by melting a homogeneous mixture of reagentgrade $CaCO_3$, dolomite, SiO_2 and Al_2O_3 at 1400°C for 1 hour in porcelain crucibles and the melts casted on a steel plate. Powder X-ray diffraction (XRD) analysis of the as-quenched glasses confirmed them to be vitreous.

The as-quenched glasses were ground to fine particle size (<20 μm) and stored in an oven at 120°C to prevent moisture attack until used for DTA measurements. The fine particle size was chosen to get rid of any eventual bulk crystallization [9].

The DTA (Netzsch STA 409) measurements were performed using about 20 mg of glass sample in a covered platinum crucible in a static atmosphere of air. A blank run was collected using calcined kaolin as sample and reference material; then the specimens were crystallized in the DTA equipment at different heating rates, 2, 5, 10 and 20 $deg\cdot min^{-1}$, and the curve recorded and corrected with the blank run. Non-isothermal experiments were performed in order to extend the temperature range of the measurements beyond that accessible to isothermal experiments. In fact many crystallization processes occur too rapidly to be measured under isothermal conditions because of transients inherently associated with the instrument. In this respect a study of crystallization kinetics under non-isothermal conditions was desirable and, beside, the question of zero-time of the isothermal kinetic approach is avoided.

Results and Discussion

The crystallization occurred at about 950°C and appeared as a single exothermic peak on the DTA curve, Fig. 1.

Although the measurements have been performed in non-isothermal conditions, the crystallization process was approximately completed (over 90%) for all the studied compositions as shown by XRD patterns collected on powdered samples before and after the peak temperature, Fig. 2.

The Kissinger equation

The DTA data were analysed primarily using the Kissinger equation [1]:

$$\ln(\Phi / T_p^2) = - E_k/RT_p + \text{const.} \qquad (1)$$

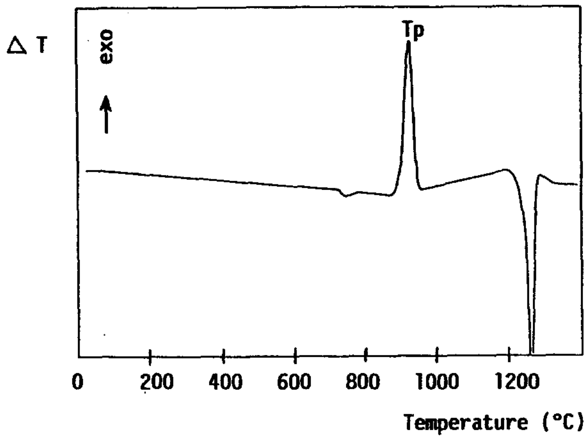

Fig. 1 Complete DTA curve of glass of composition A recorded at 10 deg·min^{-1}

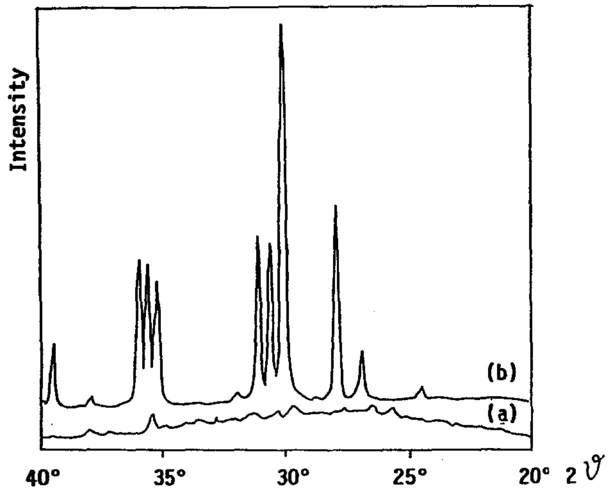

Fig. 2 Powder XRD patterns of glass of composition A: (*a*) before 900°C and (*b*) after 1000°C

where Φ is the heating rate (deg·min^{-1}), T_p is the maximum temperature of the exothermic crystallization peak, R is the gas constant (1.9872 cal·mol^{-1}·K^{-1}) and E_k is the activation energy for crystallization (cal·mol^{-1}). For sake of precision it should be pointed out that Matusita and Sakka [2–3] have stated that Eq. (1) can be used when the crystals grow on a fixed number of nuclei, while during a non-isothermal DTA measurement some corrections should be made:

$$\ln(\Phi^n / T_p^2) = -\, mE_c/RT_p + \text{const.} \tag{2}$$

where n is related to m, the Avrami parameter, which is related to the dimensionality of crystal growth, m=1 when surface crystallization is predominant and

$m=n$ when crystallization at different heating rate occurs on a fixed number of nuclei. In addition, when surface crystallization predominates, it was suggested in several papers [2, 3, 10] to use $m=n=1$ so that Eq. (2) essentially reduces to the expression of Kissinger Eq. (1).

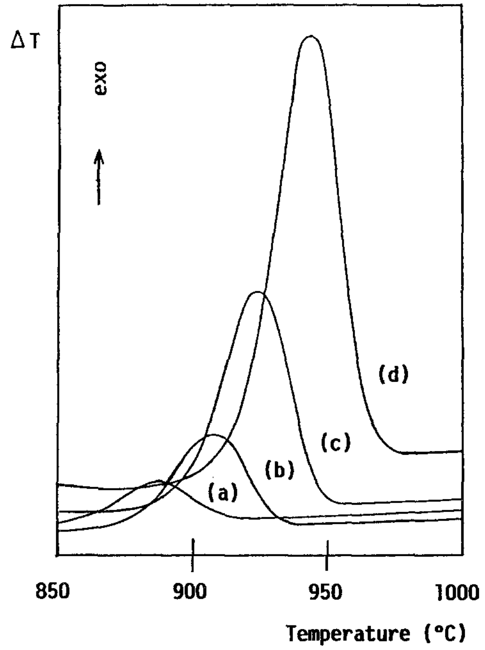

Fig. 3 DTA curves of glass of composition A at different heating rates: (a) 2 deg·min^{-1}; (b) 5 deg·min^{-1}; (c) 10 deg·min^{-1}; (d) 20deg·min^{-1}

Table 1 Kissinger equation (1) parameter values and activation energy

Φ / deg·min^{-1}	T_p/K	T_p/K
	A	B
2	1163.15	1150.15
5	1180.15	1169.15
10	1197.15	1183.15
20	1216.15	1200.15
	$r = 0.996$	$r = 0.999$
	$E_c = 117$ kcal·mol^{-1}	$E_c = 122$ kcal·mol^{-1}

Figure 3 reports a set of DTA measurements of A glass at different heating rates, where the shift in the maximum peak temperature, T_p, is clearly visible. By plotting $\ln(\Phi / T_p^2)$ *vs.* $1/T_p$, a straight line can be evaluated, from the slope of which $E_k=E_c$ can be determined. Table 1 reports the values obtained for E_c for both the compositions. The values range is that expected for glasses of these composition [9] and it can be noticed that samples from composition B show a barrier to crystallization slightly higher than composition A. This small difference was explained as due to higher number of non-bridging oxygens in glasses of composition A respect to B.

The graphical method

Secondly we tested a graphical method suggested by Pilyan *et al.* [5] to determine the activation energy of a complete transformation reaction from a single DTA curve recorded at an arbitrary heating rate (10–40 deg·min^{-1}) and particle size. The equation used is:

$$\ln \Delta t = C' - \frac{E_G}{RT} \tag{3}$$

where C' is a constant and T is the temperature (K) corresponding to a given value of Δt, which is the deviation from the baseline; R is the gas constant and E_G the activation energy of the chemical reaction.

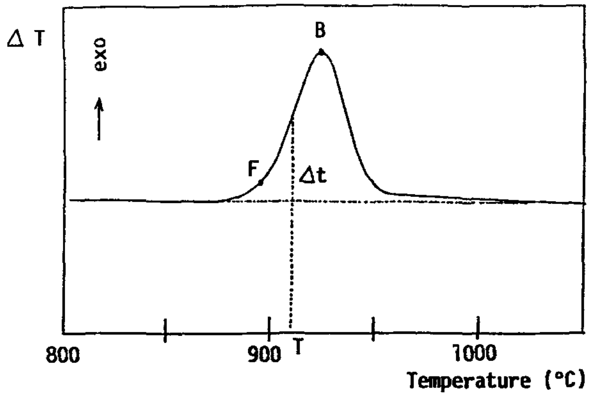

Fig. 4 DTA curve of glass of composition A at 10 deg·min^{-1} showing the various attributes of the thermal effect. For explanation see text

The Δt values are taken directly from the DTA curve in unit length (cm or mm), from point F to the point corresponding to the crystallization degree $\alpha=0.4$ of the curve [11], Fig. 4. The value of α was evaluated by computer as the ratio of the two area values So and S. In Table 2 are reported for both the compositions the values of Δt and T obtained from different heating rates and the activation energies calculated from the straight line equation. There is almost no dependence on the heating rate, but the values are almost the double of those obtained with the first method, so that in the relationship [10]:

$$E_c = n/m E_G$$

Table 2 Graphical method values from Eq. (3)

Composition A	T/K	t/cm	Composition B	T/K	t/cm
20 deg·min^{-1}	1190.35	1.35	20 deg·min^{-1}	1186.55	2.45
	1193.55	2.08		1187.65	2.55
	1196.45	2.62		1189.95	3.12
	1199.35	3.25		1191.55	3.55
	1202.75	4.22		1193.65	4.10
	1204.25	4.85		1194.95	4.60
	1206.55	5.60			
	1208.25	6.25			
r = 0.995			r = 0.998		
E_G = 236 kcal/mol			E_G = 216 kcal/mol		
10 deg·min^{-1}	1171.75	1.80	10 deg·min^{-1}	1162.15	1.80
	1174.85	2.40		1165.55	2.50
2.50	1177.45	3.05		1168.15	3.20
	1179.05	3.75		1170.85	3.70
	1180.55	4.22		1172.15	4.20
	1182.95	5.20		1173.05	4.80
	1185.35	6.10		1174.55	5.50
	1187.05	6.70		1175.85	6.10
	1189.35	7.50		1177.45	6.60
				1178.55	7.10
r = 0.993			r = 0.997		
E_G = 230 kcal/mol			E_G = 230 kcal/mol		
5 deg·min^{-1}	1159.05	1.70	5 deg·min^{-1}	1147.55	1.40
	1162.95	2.50		1150.85	2.00
	1164.95	3.10		1152.95	2.52
	1167.75	3.90		1155.75	3.10
	1170.15	4.40		1158.35	3.85
				1160.35	4.55
				1161.95	5.46
				1163.25	5.90
				1164.55	6.20
r = 0.994			r = 0.997		
E_G = 236 kcal/mol			E_G = 233 kcal/mol		

where *n* is the Avrami parameter and m depends on the dimensionality of crystal growth, the ratio *n*/*m* is between 0.5 and 0.7.

The DDTA method

This method can be applied to surface crystallization when there is the possibility of recording a simultaneous derivative curve, DDTA, together with DTA measurements. The equation suggested by Branda *et al.* [6] for the specific case of surface nucleated glasses is the following:

$$\frac{E_M}{R}\left(\frac{1}{T_{f1}}-\frac{1}{T_{f2}}\right)=1.59 \tag{4}$$

where E_M is the activation energy, R is the gas constant, T_{f1} (K) is the DDTA peak corresponding to the first inflection point of the DTA curve and T_{f2} (K) is the second inflection point (Fig. 5). Table 3 reports the parameters of Eq. (4) applied to the DDTA curve at different heating rates for the two compositions. In this case the oscillation of E_M due to the heating rate is larger than for the graphical

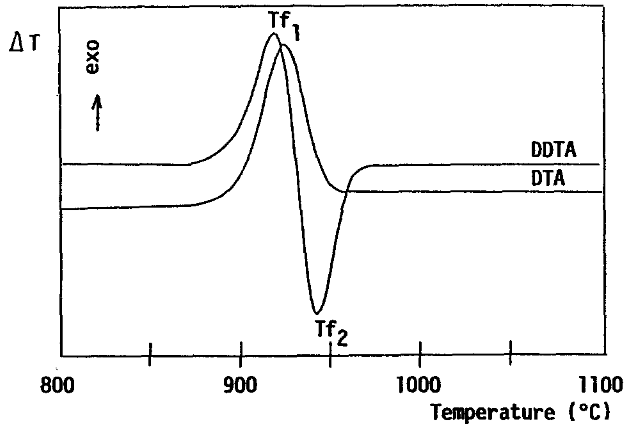

Fig. 5 DTA and DDTA curves of glass of composition A recorded at 10 deg·min^{-1}

Table 3 Graphical method values from Eq. (4)

Φ / deg·min^{-1}	T_{f1}/K		T_{f2}/K		E_M/kcal·mol^{-1}	
	A	B	A	B	A	B
5	1169.25	1165.35	1196.75	1179.65	161	304
10	1191.05	1181.65	1214.05	1197.75	199	278
20	1214.75	1201.15	1239.25	1221.15	194	232

method, but the main difference is between glasses of composition A and of composition B. Again the correction n/m=0.5 should be used to compare these results with those obtained from Eq. (1).

Conclusions

In the investigated glassy system $MgO–CaO–Al_2O_3–SiO_2$, where crystallization is surface nucleated, the values of activation energy obtained by Kissinger method are in the range of those obtained from other authors for similar glassy compositions, while the other methods tested show much higher values, Table 4.

Table 4 Activation energy for crystal growth in MgO-CaO-Al_2O_3-SiO_2 glasses

Composition	E_c/kcal·mol^{-1}	E_G/kcal·mol^{-1}	E_M/kcal·mol^{-1}
A	117	234	185
B	122	226	271

The two single-peak methods give some oscillation in the values of activation energy with the heating rate used for DTA registration, even though no trend could be figured out, as reported by others [10]. The values need to be corrected of a coefficient $n/m = 0.5$ or $n/m = 0.7$. A tentative explanation for this correction can be given considering that the Avrami parameter, n, and m changes with number of nuclei and the dimensionality of the crystallites. Different authors report $n = m = 1$ for surface nucleated glasses, but in this case the fixed number of nuclei, $n = 1$, is correlated with a bidimensional crystal growth, $m = 2$.

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References

1 H. E. Kissinger, J. Res. Natl. Bur. Stand. (U.S.), 57 (1956) 217; Anal. Chem., 29 (1957) 1702.
2 K. Matusita, S. Sakka and Y. Matsui, J. Mater. Sci., 10 (1975) 961.
3 K. Matusita and S. Sakka, Phys. Chem. Glasses, 20 (1979) 81; J. Non-Cryst. Solids, 38–39 (1980) 741.
4 N. K. Chakraborty, S. K. Das, S. K. Niyogi and R. L. Thakur, Cent. Glass Ceram. Res. Inst., Bull., 21 (1974).

5 G. O. Piloyan, I. D. Ryabchikov and O. S. Novikova, Nature, 212 (1966) 1229.
6 F. Branda, A. Buri, A. Marotta and S. Saiello, J. Mater. Sci., 17 (1982) 105.
7 T. Ozawa, Polymer, 12 (1971) 150.
8 D. W. Henderson, J. Non-Cryst. Solids, 30 (1971) 301.
9 C. Leonelli, T. Manfredini, M. Paganelli, P. Pozzi and G. C. Pellacani, J. Mat. Sci., 26 (1991) 5041.
10 X. J. Xu, C. S. Ray and D. E. Day, J. Amer. Ceram. Soc., 74 (1991) 909.
11 J. Šestak, Phys. Chem. Glasses, 6 (1974) 137.

Zusammenfassung — Vorliegende Arbeit untersucht mittels thermoanalytischen Untersuchungen die Berechtigung von drei verschiedenen Methoden zur Ermittlung der Aktivierungsenergie der Kristallisation bei Gläsern mit Oberflächen-Kristallisationskeimen im System MgO–CaO–Al_2O_3-SiO_2, wobei Anorthit- und Diopsidkristalle ausgeschieden werden. Die anhand der Kissinger-Gleichung erhaltenen Werte für die Aktivierungsenergie der Kristallisation sind vergleichbar mit denen, die von anderen Autoren für ähnliche Glassysteme erhalten wurden: 90-150 kcal/mol. Die Ergebnisse der kinetischen Analyse mittels der Einfach-Kristallisationspeak Methode sollten korrigiert werden, indem man die Dimensionalität des Kristallwachstums berücksichtigt.